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# ***OAR Box 1219***

*Prepped by Ollie Stewart*

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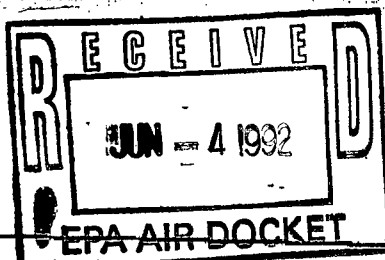
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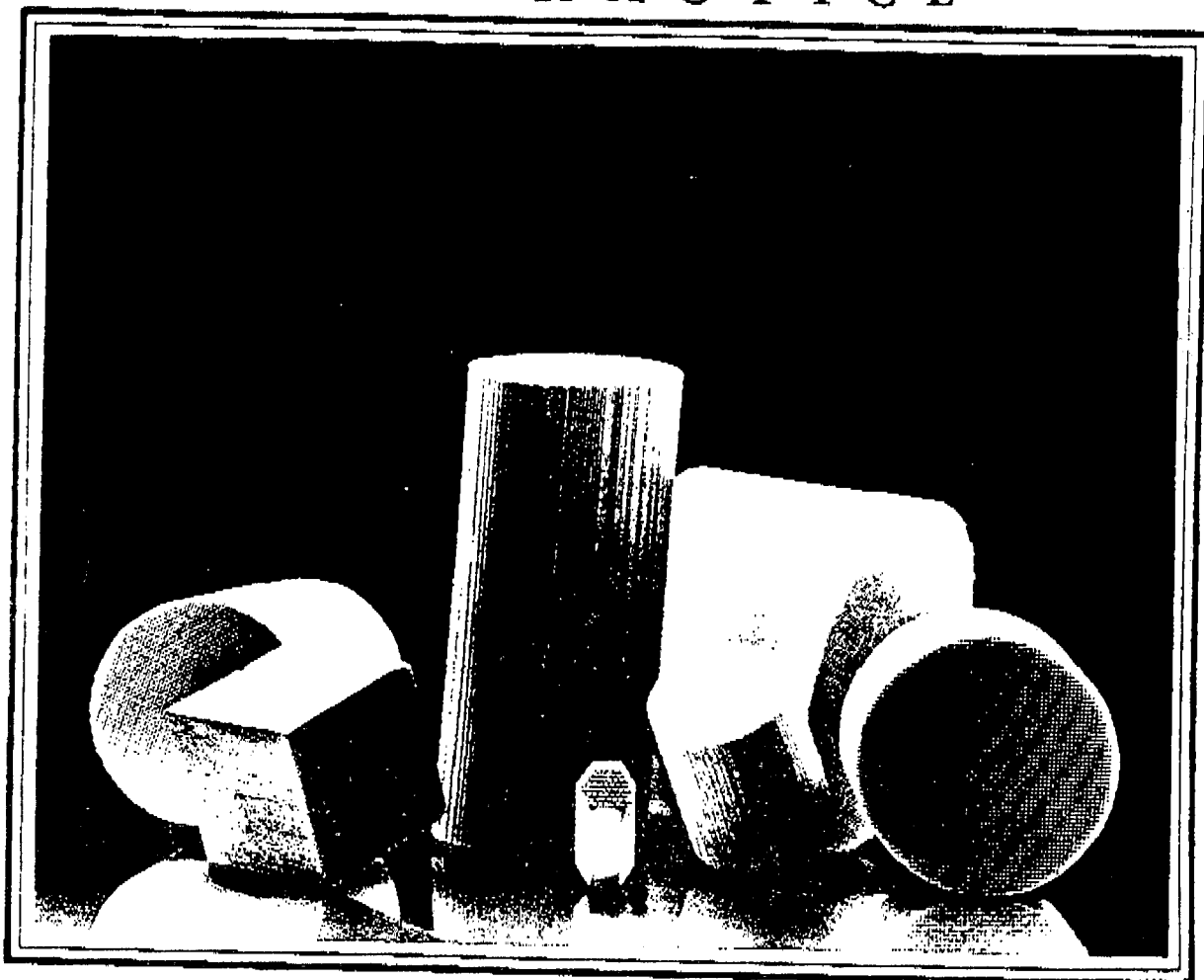
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***Docket Number:***

**A-91-46**

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# HETEROGENEOUS CATALYSIS · IN PRACTICE ·



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OPTIONAL FORM 99 (7-90)

<b>FAX TRANSMITTAL</b>		# of pages <b>12</b>
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GENERAL SERVICES ADMINISTRATION

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## ATMOSPHERIC POLLUTION CONTROL

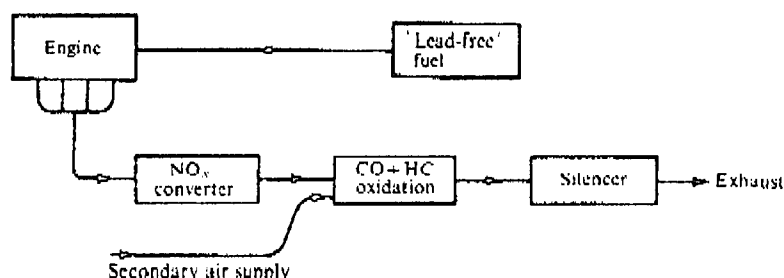


FIG.13.3. Diagrammatic representation of a catalytic system for treating ICE emissions.

first achieved by a dual-bed system (see Fig. 13.3) in which a rich mixture was first treated with a reduction catalyst (again platinum or a mixture of metals); the exhaust then passed to a second bed containing an oxidation catalyst and into which additional air was fed to ensure complete combustion. Such a procedure is clearly wasteful of fuel. The latest concept is the *three-way catalyst*, which operates at close to the stoichiometric ratio (Fig. 13.2); this is maintained by using a closed-loop feedback system in which the concentration of oxygen passing into the engine is continuously monitored by a conducting solid electrolyte. A combination of platinum and ruthenium was first tried, but it was found that the latter was gradually lost as the volatile tetroxide during lean excursions. Platinum and rhodium are now the metals of choice. The effects of small departures from the stoichiometric ratio can be partly cancelled by incorporating an 'oxygen storage' agent: this is a transition metal oxide that adsorbs oxygen when conditions change from rich to lean, and reverts to the lower oxide when they again become rich.

The final challenge is to overcome the problem of lead toxicity. Lead is a well-known poison of metallic catalysts, and, to date, petrol of low lead content has necessarily been used. The size of the problem is shown by the following rough calculation. A car travelling 16 000 km per year and doing 14.2 m l<sup>-1</sup> (40 mpg) consumes 1127 litres of petrol per year: this may contain about 0.55 g of lead per litre, so the total burden of lead passing through the catalyst containing at most a few grams of precious metal is 620 g. Nevertheless, steady progress is being made towards the design of a system that will be 'lead-tolerant'.

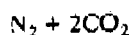
## QUESTIONS

- 13.1. What were the factors determining that photochemical smog should first have been identified in Los Angeles? Two are mentioned in the text: there are at least two others.

## TION CONTROL

lytic methods for completing the oxides.  
of using a catalyst to achieve the challenging one. Let us first list

by its reactions with carbon by a reaction such as



el not needed to achieve this and carbon dioxide.  
erate at the lowest possible igh in the first few seconds of e effective at normal operating ig on the distance of the catalyst withstand for short periods the 270 K) that might arise during

he time it takes for the vehicle to , whichever is the shorter time. the desired conversions at space volume of catalyst bed per hour. ditions of air fuel ratios that are sition of the gas entering the are never constant.

without any attention by skilled y resuscitation.

well is a major triumph for the ll whose talents have contributed s a more impressive technical cess such as catalytic reforming, alyst operates are subject to tight

tly contradictory aims of  $NO_x$  l oxidation can be achieved. The h the air fuel ratio admitted to the there is a deficiency of air with rich conditions), the combustion  $O_x$  formation is correspondingly r monoxide and unreacted fuel. ean conditions,  $NO_x$  formation is r than at the stoichiometric value, there is still some unburnt fuel. e, the reductants are in excess of

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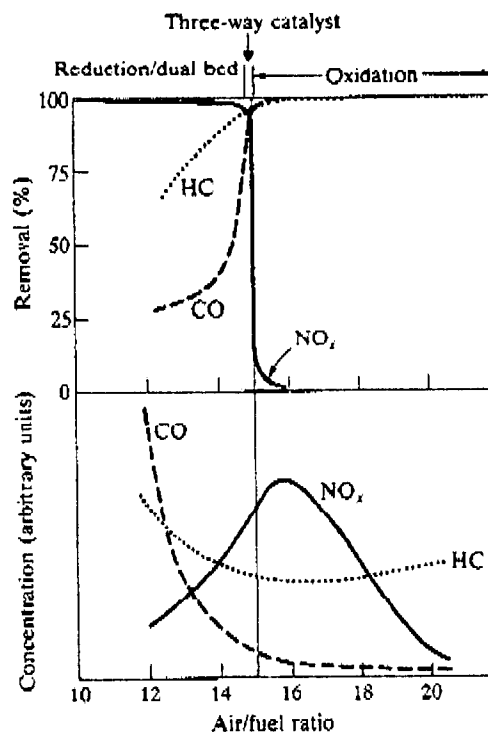


FIG. 13.2. Dependence upon air/fuel ratio of concentrations of pollutants formed in the ICE (lower part) and on the extent of their removal with the catalyst system named at the top (upper part). HC = unburnt hydrocarbons.

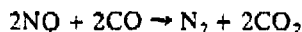
the  $NO_x$  and the removal of the latter is possible with a suitable catalyst. Not all of the reductants are needed, however, and the excess would have to be vented or further treated. Driving continuously under rich conditions is moreover uneconomic. Above the stoichiometric ratio, the only treatment possible is to oxidize the reductants, leaving the  $NO_x$  essentially untouched. These possibilities are illustrated in the upper part of Fig. 13.2.

Historically, the first solution attempted was the oxidation. Platinum, either alone or admixed with other noble metals, supported on a ceramic monolith, gave 'light-off' of the reductants at about 520 K. This is a phenomenon in which the conversion rises from a low value to almost completion for an apparent temperature increase of only a few Kelvin: it occurs when the heat of reaction cannot be removed from the catalyst as fast as it is liberated. Increasing stringency of legislative standards (Table 13.2), however, soon necessitated lowering the  $NO_x$  emissions. This was

however, we confine our attention to catalytic methods for completing the oxidation and for removing the nitrogen oxides.

It may be said at once that the problem of using a catalyst to achieve the desired ends has been a most difficult and challenging one. Let us first list exactly what has to be done.

- (1) It is required to remove the  $\text{NO}_x$  by its reactions with carbon monoxide or unburnt hydrocarbons, by a reaction such as



- (2) Carbon monoxide and unburnt fuel not needed to achieve this purpose must be oxidized to water and carbon dioxide.
- (3) The catalyst should start to operate at the lowest possible temperature, since emissions are high in the first few seconds of engine running, and should also be effective at normal operating temperatures (570–770 K, depending on the distance of the catalyst from the manifold), and be able to withstand for short periods the much higher temperatures (about 1270 K) that might arise during engine malfunction.
- (4) The catalyst must work properly for the time it takes for the vehicle to travel 50 000 miles, or for five years, whichever is the shorter time.
- (5) It must be active enough to produce the desired conversions at space velocities up to 150 000 volumes per volume of catalyst bed per hour.
- (6) It must do all these things under conditions of air fuel ratios that are continuously changing; the composition of the gas entering the catalyst, and hence its temperature, are never constant.
- (7) It must survive without maintenance, without any attention by skilled or unskilled persons, and without any resuscitation.

That these ends have been achieved so well is a major triumph for the catalyst manufacturers and is a credit to all whose talents have contributed to success. In its way, it is perhaps a more impressive technical achievement than a major industrial process such as catalytic reforming, where the conditions under which the catalyst operates are subject to tight control.

We now examine how the apparently contradictory aims of  $\text{NO}_x$  reduction and carbon monoxide and fuel oxidation can be achieved. The concentrations of the pollutants vary with the air fuel ratio admitted to the cylinder, as shown in Fig. 13.2. When there is a deficiency of air with respect to the stoichiometric ratio (i.e. in rich conditions), the combustion temperature is below the maximum,  $\text{NO}_x$  formation is correspondingly low and the main products are carbon monoxide and unreacted fuel. When there is an excess of air, i.e. in lean conditions,  $\text{NO}_x$  formation is again low because the explosion is cooler than at the stoichiometric value, carbon monoxide formation is low but there is still some unburnt fuel. Below the stoichiometric ratio therefore, the reductants are in excess of

FIG. 13.2  
in the ICE  
named at

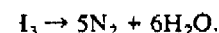
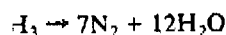
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13.2), ho

## POLLUTION CONTROL

The scrubber is heated by heat exchange from the reactor. The minimum inlet depends upon the fuel used (hydrogen, K; methane 750 K). A great deal of heat of the fuel, and this has to be used (by energy for the process to be economic. For as stream there is a temperature rise of the fuel, or about 130 K when a effect puts a limit on the amount of oxygen stage.

are active as catalysts for the reduction reaction has been thoroughly studied. of catalyst is a platinum-coated ceramic in section 7.1. A monolithic structure is chosen because of its strength, thermal flow.

the use of ammonia as a reductant. reacts with  $\text{NO}_x$  in preference to oxygen



is eliminated, ammonia is an expensive different types of catalyst have however for these reactions: these include (platinum and ruthenium), copper-exchanged zeolite metal oxides, of which vanadia, seems to be best.

## Exhaust gases

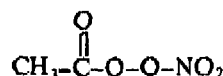
How important the internal combustion atmospheric pollution. The magnitude of the following estimated annual emissions from a vehicle travelling 10 000 miles: incomplete combustion of the fuel, 150 kg of nitrogen oxides formed from the hydrocarbons emitted, 65% arises from the crank-case blowby (20%), the loss from the fuel tank (6%). Substances like oil and cylinder-ring wear naturally being undergone chemical transformation and alkyls appear as the halides, oxides or chemical consequences of the additives are,

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and in the case of lead they are almost certainly serious, they are not susceptible to treatment by catalytic means. Diesel engines, if properly tuned and operated, are inherently cleaner than ICEs, although they represent a hazard, especially when used in confined spaces.

Awareness of the hazards of pollution from the ICE arose through the gradual recognition of their responsibility for 'photochemical smog', first detected in the Los Angeles area in the early 1940s. Because the city is enclosed on three sides by high ground, and since vertical air circulation is often restricted because of a temperature inversion, it is particularly prone to the phenomenon; but it has since been detected in Tokyo and some other large cities, although it is fortunately not a problem in Britain. Photochemical smog is formed by a complex series of reactions between hydrocarbons, nitrogen oxides, and oxygen catalysed by sunlight. It affects plant growth, and at low concentrations ( $\sim 0.1$  p.p.m.) it is irritating to the eyes, while at higher concentrations ( $> 0.6$  p.p.m.) it affects pulmonary functions. The principal noxious agent is peroxy-acetyl nitrate:



The situation led to the introduction, first in California and later throughout the United States, of legislation to limit ICE emissions. Standards have been progressively raised, as Table 13.2 shows: those expected to apply in Europe are likely to be at least as severe.

Many solutions to these problems have been proposed. There have been radical solutions, such as changing to a cleaner fuel (e.g. propane or methanol or even hydrogen); a lower combustion temperature would result in lower  $\text{NO}_x$  emissions. Other suggestions have included a complete re-design of engine operation (e.g. the Wankel engine), and inclusion of a catalyst within the cylinder to give easier combustion. In the following,

TABLE 13.2

United States federal legislation on emissions from cars

Model year	Emission limits ( $\text{g mile}^{-1}$ )		
	Hydrocarbons	$\text{NO}_x$	CO
1973	3.4	3	39
1975	1.5	3.1	15
1978	0.41	2	7
1981	0.41	1	3.4
1983*	0.41	0.7	7

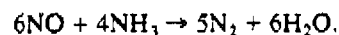
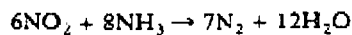
\*These values apply in the State of California, U.S.A.

*Heterogeneous Catalysts, G.C. Bond*  
*Principles & Applications 2nd ed. 1987*  
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In practice the effluent from the scrubber is heated by heat exchange with the hot gas emerging from the reactor. The minimum inlet temperature for high conversion depends upon the fuel used (hydrogen, 470 K; propane and butane, 520 K; methane 750 K). A great deal of heat is also liberated by the combustion of the fuel, and this has to be used (by means of a turbine) to generate energy for the process to be economic. For every per cent of oxygen in the gas stream there is a temperature rise of about 160 K when hydrogen is the fuel, or about 130 K when a hydrocarbon fuel is used. This effect puts a limit on the amount of oxygen that can be removed in a single stage.

Many of the Group VIII metals are active as catalysts for the reduction of  $\text{NO}_x$ , and the mechanism of the reaction has been thoroughly studied. One of the most successful types of catalyst is a platinum-coated ceramic honeycomb of the kind described in section 7.1. A monolithic structure is particularly useful in this application because of its strength, thermal stability and low resistance to gas flow.

Mention was made above of the use of ammonia as a reductant. Ammonia, unlike the other fuels, reacts with  $\text{NO}_x$  in preference to oxygen according to the equations



Although the reaction with oxygen is eliminated, ammonia is an expensive material to use as a fuel. Several different types of catalyst have however been reported to be active for these reactions: these include alumina-supported metals (platinum and ruthenium), copper-exchanged zeolites, and a number of transition metal oxides, of which vanadia, supported on alumina or titania, seems to be best.

### 13.5. The control of motor-vehicle exhaust gases

We have already seen in Table 13.1 how important the internal combustion engine (ICE) is as a source of atmospheric pollution. The magnitude of the problem is further stressed by the following estimated annual emissions from a medium-sized (2-litre) engine in a vehicle travelling 10 000 miles: 700 kg of carbon monoxide from incomplete combustion of the fuel, 150 kg of hydrocarbons and 130 kg of nitrogen oxides formed from the components of air. Of the hydrocarbons emitted, 65% arises from the exhaust gas, and the remainder from crank-case blowby (20%), the carburettor (9%) and evaporation from the fuel tank (6%). Substances added to petrol to improve octane rating and cylinder-ring wear naturally appear in the exhaust, usually having undergone chemical transformation in the cylinder: thus the lead tetra-alkyls appear as the halides, oxides or sulphate. Whatever the environmental consequences of the additives are,